

✿ Triglyceride Specific Heat Determined by Differential Scanning Calorimetry

J.W. HAMPSON and H.L. ROTHBART, Eastern Regional Research Center,¹
Philadelphia, PA 19118

ABSTRACT

The specific heats of the three polymorphic forms of trilaurin, trimyristin, tripalmitin and tristearin have been determined by differential scanning calorimetry (DSC). Results from -90 to +100°C for the triglycerides were obtained and compared with the literature values determined by classical methods.

INTRODUCTION

In a previous paper (1), heats of fusion data for the beta form of trilaurin, trimyristin, tripalmitin, and tristearin were presented along with several standards. The data were obtained by using the differential scanning calorimetric (DSC) technique. This report presents the specific heat data from -90 to 100°C for the three common forms of these four triglycerides using the DSC method. Comparisons are made with data previously reported in the literature obtained by other procedures.

The nomenclature used herein to identify the polymorphic forms is that used by Lutten (2). The three forms are designated as α , β' , and β in increasing order of their melting point.

Differential scanning calorimetry as a method for determining specific heat has been discussed by O'Neill (3) and several workers have used the method for polymers (4,5), liquid crystals (6), organic liquid reactor coolants (7), and interfaced to a computer (8). However, no reports have been given applying this technique to pure triglycerides. Indeed the only extensive specific heat study of triglycerides seems to be the work of Charbonnet and Singleton in 1947 (9). At that time the purity of the materials was not well known as gas liquid chromatography (GLC) and thin layer chromatography (TLC) were not available. Also the specific heat of the β' forms was not shown and the α form data for trilaurin was also not shown.

The purpose of our research was: (a) to determine the specific heat of the three common forms of the four triglycerides, filling in data not present in the literature; (b) to determine the accuracy of the DSC technique; and (c) to ascertain if there are any obvious specific heat anomalies at low temperature which would be indicative of a second-order transition, as has been pointed out by Chapman (10).

EXPERIMENTAL

Materials

Sapphire, 32.620 mg (Union Carbide sample supplied by Perkin-Elmer) was used to standardize the method. Triglycerides (99+% Applied Science Laboratories) were shown to be greater than 99% pure by gas liquid and thin layer chromatography. Mercury, ice and indium were used to calibrate the temperature scale.

Method

Calorimetry. Glyceride samples of 10-23 mg were weighed

in nonvolatile type containers (Perkin-Elmer) with their lids on a Cahn Electrobalance (Model RG) to ± 0.005 mg.

A sample was placed in the Perkin-Elmer DSC 1B and covered with an aluminum dome. A similar assembly without sample served as the reference. Heating rate and sensitivity were 10 K/min and range 4, respectively. Nitrogen was passed through the heating chamber at atmospheric pressure and a flow of 13.3 mL/min measured at the bypass outlet. The low-temperature-head assembly (Perkin-Elmer) filled with liquid nitrogen was used to cool the samples and detector.

Before liquid nitrogen was added to the low-temperature head, the instrument was purged with dry nitrogen gas for 5 min to remove any trace of moisture. Liquid nitrogen was then added and the β form of the triglyceride prepared by crystallization from solvent was allowed to cool to ca. 181 K. Measurements were made on the reheated sample to 381 K. The melt was cooled as rapidly as possible (quenched) to ca. 180 K, which resulted in the α form of the triglycerides (10). The β' form of the triglycerides was obtained by quenching the melt to 2-5 K above the mp of the α form and maintaining the materials at that temperature until crystallization, followed by quenching to 180 K (11).

The preliminary stages of the work involved manual operation of the equipment and the data were obtained according to the recommended procedures (3,12).

RESULTS AND DISCUSSION

The specific heat data were obtained by on-line computer acquisition and processing and is included in Tables I-IV. The data are obtained for the β , α , β' crystal forms in that order as the β and α forms are much easier to obtain. When a crystal form undergoes melting or recrystallization, it produces a peak and makes it impossible to measure specific heat at that temperature. These ranges are indicated by dashes in Tables I-IV. Each crystal form had a distinctly different thermal profile and melted in the region described in the literature.

Data comparison with the literature is shown in Table V. The average difference is 5% with the best agreement found for tripalmitin (3% maximum difference) followed by trilaurin, trimyristin and tristearin in that order. The least agreement found is for the tristearin β form at low temperatures where the difference is ca. 15%. The results in this paper show that reliable triglyceride specific heat measurements can be made by the DSC method.

Figure 1 shows that the specific heat of the three forms of tristearin increases in the order β , β' , α . However, at low temperatures, 190 K (-83°C), the specific heat is very close for the three forms. An extrapolation of the data in Tables I-IV shows that below 150 K the α and β form specific heat for each triglyceride is about the same. At ca. 210 K (-63°C) the specific heat, particularly of the α form, begins to increase substantially over the specific heat of the β form. It has been shown (13) that in this temperature range there is a reversible sub- α to α form second-order transition. Since second-order transitions sometimes produce large peaks in

¹Agricultural Research Service, US Department of Agriculture.

TRIGLYCERIDE SPECIFIC HEAT BY DSC

TABLE I

Tristearin Specific Heat (cal/g/K)

Temperature (K)	Form		
	β	β'	α
180	0.219	0.222	0.222
190	0.220	0.229	0.229
200	0.226	0.239	0.242
210	0.240	0.260	0.266
220	0.252	0.274	0.279
230	0.265	0.294	0.309
240	0.268	0.304	0.330
250	0.285	0.326	0.356
260	0.299	0.338	0.375
270	0.321	0.373	0.402
280	0.327	0.382	0.419
290	0.359	0.412	0.454
300	0.355	0.422	0.468
310	0.374	0.462	0.510
320	0.398	0.499	0.577
330	0.419	—	—
340	0.437	—	—
350	—	0.489	—
360	0.474	0.495	0.507
370	0.496	0.507	0.507
380	0.497	0.500	0.500

TABLE III

Trimyristin Specific Heat (cal/g/K)

Temperature (K)	Form		
	β	β'	α
190	0.264	0.286	0.294
200	0.276	0.308	0.319
210	0.273	0.301	0.324
220	0.291	0.321	0.341
230	0.304	0.332	0.360
240	0.314	0.349	0.375
250	0.320	0.362	0.393
260	0.341	0.381	0.419
270	0.347	0.395	0.433
280	0.359	0.420	0.458
290	0.383	0.451	0.503
300	0.392	0.473	0.534
310	0.422	0.508	—
320	0.442	—	—
330	—	—	—
340	—	—	—
350	—	0.505	—
360	0.534	0.532	0.534
370	0.533	0.535	0.535
380	0.534	0.540	0.534

TABLE II

Tripalmitin Specific Heat (cal/g/K)

Temperature (K)	Form		
	β	β'	α
190	0.240	0.254	0.257
200	0.264	0.280	0.293
210	0.270	0.303	0.315
220	0.283	0.314	0.329
230	0.286	0.310	0.331
240	0.300	0.325	0.357
250	0.307	0.334	0.376
260	0.321	0.354	0.397
270	0.341	0.374	0.418
280	0.353	0.396	0.440
290	0.375	0.433	0.474
300	0.393	0.462	0.514
310	0.424	0.500	—
320	0.455	0.544	—
330	0.472	—	—
340	—	—	—
350	—	—	—
360	0.537	0.534	0.532
370	0.534	0.533	0.534
380	0.544	0.548	0.544

TABLE IV

Trilaurin Specific Heat (cal/g/K)

Temperature (K)	Form		
	β	β'	α
190	0.249	0.252	0.273
200	0.279	0.279	0.305
210	0.261	0.275	0.299
220	0.278	0.292	0.322
230	0.284	0.295	0.335
240	0.294	0.312	0.350
250	0.305	0.327	0.373
260	0.319	0.342	0.386
270	0.331	0.352	0.414
280	0.342	0.365	0.438
290	0.364	0.401	—
300	0.385	0.428	—
310	0.409	—	—
320	—	—	—
330	—	—	—
340	0.498	0.506	0.496
350	0.516	0.522	0.516
360	0.513	0.517	0.513
370	0.515	0.515	0.515
380	0.523	0.519	0.523

TABLE V

Triglyceride Specific Heat Comparison (cal/g/K)

Temperature (K)	Tristearin	Tripalmitin	Trimyristin	Trilaurin
		β Form		
200	.225(.261) ^a	.263(.265)	.276(.264)	.278(.269)
250	.285(.321)	.307(.317)	.320(.322)	.305(.325)
		α Form		
200	.241(.283)	.293(.291)	.319(.291)	.304(-)
250	.355(.378)	.376(.378)	.393(.368)	.373(-)
		Liquid		
370	.507(.542)	.534(.539)	.534(.534)	.515(.530)

^aValues in parenthesis are from the literature (9).

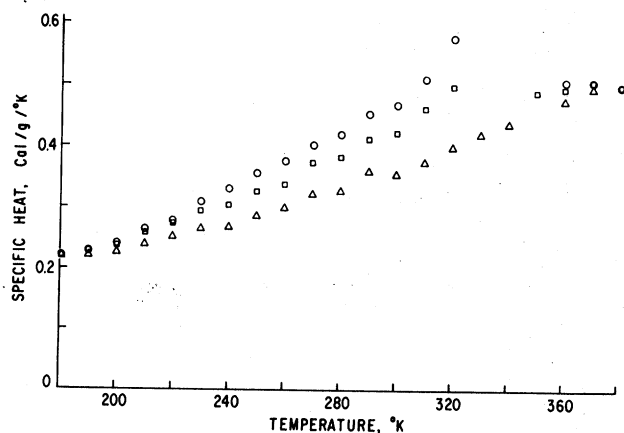


FIG. 1. Tristearin specific heat beta Δ , beta prime \square , and alpha form \circ .

the specific heat vs temperature curve, a peak was looked for in the data presented in this report, but it was not found. Nor were any peaks or anomalies found in the actual recorder traces.

The α form is a hexagonal crystal whose carbon chains are known to rotate somewhat about their axis (10). This rotation would be expected to contribute to the specific heat. It would seem from Figure 1 that this rotation substantially increases at ca. 210 K (-63 C), and may explain why there is a large difference in the specific heat of the α form over the β form as the temperature increases. At 260 K, α tristearin specific heat is 25% greater than the β form. At 300 K, the α form is about 32% greater than the β .

The data in this paper and an interpretation of the litera-

ture tend to confirm that at low temperatures there is an α to sub- α second-order transition. But the transition is gradual and not limited to a narrow temperature range. Apparently, at low temperatures the α form stops most of its rotation and takes up fixed positions. This explains the decrease in specific heat, the appearance of a new X-ray short spacing as the α form is cooled (14), and the appearance of a doublet in infrared spectroscopy (10).

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